STUDIES IN SOIL CATALYSIS.

BY

M. X. SULLIVAN AND F. R. REID,

Scientists in Soil Fertility Investigations.

LETTER OF TRANSMITTAL.

Sir: I have the honor to transmit herewith the manuscript of a scientific paper entitled "Studies in Soil Catalysis," by Dr. M. X. Sullivan and Mr. F. R. Reid, of this bureau. This article forms an important contribution on some little-understood factors in soil fertility. The mild but effective oxidation shown to exist in soils has a very appreciable effect in aiding the decomposition of organic matter in the soil. Catalysis is a factor of importance which is closely associated with soil oxidation. The importance of the organic constituents of the soil makes these results especially interesting, and the material throws additional light upon the question of soil fertility. I have, therefore, the honor to recommend that this article be published as Bulletin No. 86 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

The present paper is one of a series reporting upon the biochemical factors in soils. The causes of fertility and infertility of our agricultural lands are complex, not simple as some would have us believe, and it is only by a study of the chemical, physical, and biological activities going on in the soil that we can get a thorough insight into the problems of soil fertility. The purely chemical and physical sides have been studied quite extensively in the past; the biological side, however, but little. Whatever adds to our biochemical knowledge of soils advances and broadens our understanding of the complex problem of soil fertility. Accordingly, this laboratory has taken up a series of studies on biochemical factors in soils. Much valuable and definite information concerning the presence and properties of certain constituents of soils, produced by biochemical agencies, has already been obtained. Some of these have been shown to be harmful to plants and others decidedly beneficial. Some thirty compounds have thus far been definitely isolated and identified and through them a fairly comprehensive view of the biochemical changes which take place in soils obtained. The biochemical processes, however, by which changes are brought about are, on account of the very nature of the case, less definite and less tangible and require much further study before they can be thoroughly understood. I refer to the action of bacteria, of molds, and other life within the soil in producing chemical changes, of the activity of enzymes, and of such processes as deamidization, oxidation, reduction, and catalysis. The biochemical factors of oxidation and reduction in soils by plant roots and other powers have already received consideration in earlier bulletins and a study of the closely related subject of catalysis is given in the present paper.

Oxidation in soils is perhaps one of the most important processes in the soil and is well recognized in practical tillage. Besides the purely chemical oxidations there are the biological agencies which are perhaps the ones most persistent in soil oxidation. Among these are the oxidizing functions of bacteria, of molds, and of plant roots, and of the enzymes produced by these agencies. Oxidation by plant roots is a factor which has considerable agricultural interest, especially from the viewpoint that such oxidation is able to change the organic

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matter in the medium in which the plant is growing and that processes promoting oxidation play a large part in the best methods of soil cultivation, tillage, and crop rotation. The oxidation of organic matter in the soil is of additional interest in that the investigations of this laboratory have shown that the cause of unproductivity in certain soils is due to the presence of harmful organic matter in the soil. The beneficial effect of oxidation in such soils can be inferred from the effects of tillage, involving subdrainage and cultivation, since these operations promote aeration of the soil with subsequent increase of roots and microorganisms and an increase in the measurable oxidative property.

Valuable and necessary as are these oxidative functions in the soil, to produce sanitary surroundings for the plant and to promote decomposition of organic débris so that valuable plant nutrients may again be started on their way to produce new foodstuffs for plant and animal, an excessive amount of oxidation is, on the other hand, undesirable and dangerous to the proper functioning of the soil. Whatever induces excessive oxidation in soil, plant or animal, is undoubtedly injurious. Excessive oxidation produces or accompanies diseases in both animals and plants. In plants, chlorophyll is destroyed and a group of plant diseases are accompanied by great oxidative power of the plant juices. Strong oxidizing agents are poisonous to plant life, whether they be organic or inorganic in character. Under normal conditions such excessive oxidation, resulting in the formation of peroxide material, is probably prevented or controlled by a catalytic property inherent in vegetable and animal tissues, and this same property of preventing excessive oxidation has been found to exist in normal soil. The present paper is a contribution to this subject and throws much light upon the nature of catalysis and its correlation with soil conditions and different soil types. The paper will show that this property of catalysis is especially prominent in strong, vital soils. These various factors of oxidation, reduction, catalysis, and others still to be reported on can doubtless be all correlated in a manner which will give us still greater and more complete insight into the biochemistry of soils.

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OSWALD SCHREINER,
In charge Fertility Investigations.

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STUDIES IN SOIL CATALYSIS.

INTRODUCTION.

By soil catalysis is meant the power inherent in soils to decompose peroxides, especially hydrogen peroxide, with the liberation of oxygen as a measurable factor.

The soil, as is clearly recognized at the present day, is not merely a reservoir for the nutrients of plants, but is rather the seat of complex physical, chemical, and biological action which directly and indirectly influences fertility.

The various factors at work in soils have been extensively studied with the main stress, until recent years, upon the physical and chemical side. Within the last decade or two, however, much attention has been given to the biochemical side of soil and much valuable work has been done along this line, especially in the field of soil bacteriology. The work of soil bacteriology, however, has been limited for the most part to the study of the nitrogen problem, to denitrification, nonsymbiotic and symbiotic fixation of nitrogen, and to ammonification. On the other hand, biochemical factors in soil, such as the nature of the organic matter of soils and the change produced in soil constituents by microorganisms, the synthesis of organic compounds in soils, the presence of enzymes, the effect of plant growth on the soil and soil constituents, the physiological effect of organic soil constituents on plants, the action of fertilizers, and the oxidizing, reducing, and catalyzing powers of the soil, have received less consideration until recently in this and other laboratories. Using the methods employed in plant and animal physiology, the oxidizing power of the soil per se and in conjunction with plant growth and fertilizers was shown to be correlated more or less with the productivity of the soil in that, as a rule, soils with good oxidizing power were the productive soils, while most soils known to be of poor productivity had poor oxidizing power and that factors favoring fertility favored oxidation.[1]

Associated with the oxidizing power of plant and animal tissue is the power to decompose hydrogen peroxide with the evolution of oxygen. This property of the tissues to decompose hydrogen perox-

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[1] Bulletin 73, Bureau of Soils, U. S. Department of Agriculture (1910).

ide has been generally attributed to the enzyme catalase, and the process is known as catalysis.

New knowledge of every factor in soils is a step in advance toward a better understanding of soil fertility. Thus the study of the oxidizing power of the soil was found a fruitful field for research which threw some additional light on the problems of soil fertility. Considerable attention therefore has been given to the catalytic power of the soil in its relation to soil varieties and types, to plant growth, and to fertilizer action. These results are given in the present paper.

A catalyst, according to Ostwald,[1] is a body which alters the rate of change in a reaction. The change may be either in the direction of acceleration or retardation, and the reaction may be one that by itself proceeds rapidly or so slowly that it requires special proof to show that it is taking place at all. It is especially to the acceleration of reaction that the term catalysis is usually applied. Without going further into the discussion of the characteristics of catalytic reactions, it may be said that by the catalytic decomposition of hydrogen peroxide is meant the rapid breaking up of the hydrogen peroxide into water and oxygen in the presence of another substance. The acceleration of the decomposition of hydrogen peroxide by certain substances has long been known.

Thénard[2] early studied the catalytic decomposition of hydrogen peroxide and concluded that most bodies affect the peroxide. Some, like the acids, phosphoric, hydrofluoric, sulphuric, hydrochloric, arsenic, and oxalic, tend to increase its stability, while the metals, metallic sulphides, oxides, and carbon tend to decompose it. He noted later[3] the analogous action of the noble metals, silver and platinum, and animal tissue on hydrogen peroxide and thought it probable that its decomposition was due to the same force in each case. Berzelius[4] compared the contact action of platinum, silver, etc., in decomposing hydrogen peroxide with the action of the ferments. Schönbein[5] greatly extended these observations and pointed out that many organic substances decomposed hydrogen peroxide and found that this catalytic activity was widespread in plant and animal tissues. He found that certain poisons, especially hydrocyanic acid, exercised a similar retarding action on the decomposing power of metals and of ferments. He believed further that all ferments were able to decompose hydrogen peroxide; a belief that persisted until 1888, when Bergengrün[6] found that the fibrin ferment

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[1] Zeit. Electrochem. 7, 995 (1900–01).

[2] Ann. chim. et phys., 9, 314, 441 (1818).

[3] Ann. chim. et phys., 11, 85 (1819).

[4] Berzelius, Jahresber., 73, 237 (1836).

[5] Jour. prakt. Chem., 89, 323 (1863).

[6] Ueber die Wechselwirkung zwischen Wasserstoffsuperoxyd und verschiedenen Protoplasma-Formen. Dorpat 1888.

did not decompose the peroxide. Later Jacobson[1] showed that there is no parallel between the catalytic action of the enzymes, emulsin, trypsin, and diastase on hydrogen peroxide and their other activities and proved that enzymes might lose the catalytic power without losing their specific activities.

Spitzer[2] believed that the power to decompose hydrogen peroxide is a measure of the oxidizing power of various animal tissues. Lépinois,[3] contrary to the views of Spitzer, showed that for the various tissues there does not always exist a parallelism between the quantity of oxygen evolved from hydrogen peroxide and the intensity of oxidation of guaiacum and guaiacol.

Up to 1901 the power to decompose hydrogen peroxide was considered a more or less general property of enzymes. In 1901, however, Loew,[4] while working on the tobacco plant, found that this power of tissues is due to a special enzyme which he called catalase. He found catalase so widespread in animal and plant tissue that he decided there did not exist a group of organisms or any organ or cell which did not contain some catalase. Since Loew's discovery of the enzyme catalase the work on catalase in plant and animal tissue has been very extensive. This work has been recently summarized by Battelli and Stern.[5]

As to the function of the catalase little can be said. According to Loew,[6] Herlitzka,[7] Battelli and Stern,[8] and Shaffer,[9] the catalase of plant and animal tissue protects the tissue against excessive oxidation. Though the catalytic power is usually associated with the oxidizing power, the relation between oxidation and catalysis is by no means clear nor is the function of catalase fully understood. Indeed the only function of catalase that is known with certainty is its power to decompose hydrogen peroxide in a manner analogous to that of colloidal platinum.

The action of colloidal solutions of metals has been studied by Bredig and his coworkers,[10] by Kastle and Loevenhart,[11] Liebermann,[12] and Senter.[13]

Between the action of catalase and the different metallic catalyzers on hydrogen peroxide there is considerable resemblance. In fact

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[1] Zeit. physiol. Chem., **16,** 340 (1892).

[2] Arch. ges. Physiol., **67,** 615 (1897).

[3] Compt. rend. Soc. Biol., **51,** 401 (1899).

[4] Report 68, U. S. Department of Agriculture (1901).

[5] Ergebnisse der Physiol., **10,** 531 (1910).

[6] Loc. cit.

[7] Rend. Sci. Fis. Mat. et Nat. Real Acad. Lincei, **16,** ser 5, part 2, 473 (1907).

[8] Compt. Rend., **141,** 1044 (1905).

[9] Am. Jour. Physiol., **14,** 299 (1905).

[10] Zeit. phys. Chem., **31,** 258 (1899) : **37,** 1, 323 (1901).

[11] Am. Chem. Jour., **29,** 397, 563 (1903); Am. Jour. Physiol., **13,** 171 (1905).

[12] Arch. ges. Physiol., **104,** 119, 155 (1904).

[13] Zeit. phys. Chem., **44,** 257 (1903); **51,** 673 (1905).

Bredig considered the analogy so close that he spoke of the inorganic catalyzers such as colloidal platinum as "inorganic ferments." In other words, he considered the colloidal solutions of the metals as inorganic types of the organic ferments. Loevenhart and Kastle's work, however, showed that the analogy is probably a coincidence, since many substances act differently with the two orders of catalyzers, in that they may inhibit the one and accelerate the other. Liebermann [1] also thinks that the mechanism of the decomposition of hydrogen peroxide by colloidal platinum and by catalases of animal or vegetable origin is essentially different. According to Liebermann, active oxygen is formed in the decomposition of hydrogen peroxide by platinum, while in the case of catalase of animal and plant origin, no active oxygen is formed. The most important difference between catalase and inorganic catalyzers is, as pointed out by Loew,[2] that the action of catalase is specific while the colloidal metals not only decompose hydrogen peroxide, but also oxidize guaiac and cause reduction. Whether the inorganic catalyzers and catalase act in exactly the same way or merely in analogous ways is still an unsettled question. In both cases, the mode of action is still a matter of theory. However, the fact that a hydrogen peroxide decomposing force is present in soil is rather interesting and the study of this power should offer a fruitful field of research, either by itself or in association with other soil factors.

DECOMPOSITION OF HYDROGEN PEROXIDE BY SOILS.

As pointed out by König, Hasenbäumer, and Coppenrath,[3] soil has the power to liberate oxygen gas from hydrogen peroxide. They believed that the decomposition of the peroxide was brought about mostly by the enzyme catalase which was associated with the bacteria of the soil and to a smaller degree to inorganic colloids which behave somewhat as platinum black. Later [4] these investigators studied the hydrogen peroxide decomposing power of soil in greater detail and ascribed it as before to the enzyme existing in soils and to the colloidal action of the oxides of manganese and iron, Mn_3O_4 and Fe_2O_3. In their earlier studies they found that different soils decompose the peroxide in different degrees. Calcareous soils had the greatest activity, then clay, loam, sandy loam, and sandy soil. In their latter work they found that the power is in almost direct relation to the humus content of soils. Clay soils, however, with small humus content and large manganese content develop the larger proportional amount of gas, so that it would seem from their work that the catalytic power of the soil is dependent on both the organic and the inorganic matter.

[1] Ber. deutsch. chem. Ges., **37**, 1519 (1904).   [3] Landw. Vers-Sta., **63**, 471 (1905–6).

[2] Loc. cit.   [4] Landw. Vers-Sta., **66**, 401 (1907).

Later May and Gile made a detailed study of some Porto Rican [1] soils and concluded that the power of a soil to decompose hydrogen peroxide depends upon the catalase content, enhanced only in special cases by the colloidal action of the mineral constituents. This property they considered was a rough measure of the combined quantity of bacteria and organic matter present in the soil. The most accurate method of comparing different quantities of catalase they found to be the measurement of the rate of reaction or time required to evolve a certain volume of oxygen from a certain quantity and concentration of hydrogen peroxide.

In this laboratory, likewise, it was concluded (1) that the amount of oxygen evolved by a certain quantity of soil for a certain amount of peroxide signified little since a small amount of a catalytic agent, unless destroyed in the reaction, will decompose as much peroxide as a larger amount although at a slower rate; (2) that the best measurement of the catalytic power of soils is a measurement of the rate or the time required to evolve a certain volume of oxygen from a definite quantity and concentration of the peroxide; (3) that both the total volume of oxygen evolved and the rate of evolution should be considered in judging the relative catalytic power of soils.

The speed of the reaction between catalase and hydrogen peroxide as shown by May and Gile depends upon (1) the amount of catalase present; (2) the concentration of the peroxide used; (3) the amount of peroxide used; (4) the acidity or alkalinity of the solution in which the reaction takes place; (5) the temperature at which the reaction takes place; (6) the frequency with which the flask containing catalase and the peroxide is agitated.

METHOD OF TESTING THE CATALYTIC POWER OF SOILS.

Five grams of air-dried soil were placed in a large test tube having a capacity of 90 c. c. provided with a two-holed rubber stopper through which passed a small dropping funnel and a glass tube connecting with a gas-measuring tube. The peroxide used was a slightly acid rather stable solution containing approximately 3 per cent hydrogen peroxide by weight. Before using the peroxide it was made faintly alkaline to phenolphthalein by means of dilute sodium hydroxide. The neutralized peroxide, somewhat diluted, was dropped upon the soil by means of the funnel, and the oxygen was collected in the measuring tube. As a rule 10 c. c. of approximately $1\frac{1}{2}$ per cent hydrogen peroxide solution was used in the experiments. The criterion for the catalytic power of the soils was the time required to evolve 50 c. c. of oxygen. In the experiment each tube was shaken once every minute for 15 seconds. The results are strictly comparable

[1] Circular 9. Porto Rico Agr. Expt. Sta. (1909).

only in each experiment where the same neutralized peroxide was used and the temperature conditions were the same. No corrections were made in the volume of oxygen for variations in temperature and barometric pressure since the method was considered useful only in determining fairly wide and distinct difference in catalytic power. In the reaction between the hydrogen peroxide and soil, heat is generated. The increase in temperature varies from 2 degrees in slow catalyzers to $5\frac{1}{2}$ degrees in rapid catalyzers. The apparatus employed is shown in Plates I and II.

CATALYTIC POWER OF SOILS.

Since in certain experiments it was found that the acid of the peroxide lessened the catalytic power of the soils a high-grade neutralized peroxide was used as described in the method, given already. The catalytic power of a number of soils is given in Table I.

TABLE I.—*The catalytic power of soils.*

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	
	C.c.	*C.c*	*C.c.*	*C.c.*	*Minutes.*
Hagerstown loam plus manure	49.7	59	61	61	7.2
Hagerstown loam plus complete fertilizer	52	61	62	62	6
Hagerstown loam plus lime and manure	57	58	58	58	3.6
Hagerstown loam plus lime	63	64	64	64	3
Hagerstown loam	53	59	61	61	5.3
Clarksville silt loam, Tennessee	50	55	56	56	7
Clarksville silt loam, Kentucky	61	61	61	61	1.9
Sharkey clay	64	68	68	68	3
Volusia silt loam	30	44	57	62	21
Dutchess silt loam	37	52	61	62	14
Woodland soil, Reading, Conn	56	61	61	61	5.2
Orangeburg loam	62	64	64	64	1.3
Arlington clay loam	15	22	28	33	....

As may be seen from the table, the various soils differ considerably in catalytic power. Soils which gave the greater decomposition of the hydrogen peroxide were soils which were known to be of good productivity, while the poor soils had, as a rule, poorer catalytic power. The catalytic power and productivity, however, do not necessarily agree, since there are soils of slight catalytic power which give good crop growth. Crop production, as is well known, is dependent upon many factors, no one of which can be taken as an absolute criterion. The ability to decompose hydrogen peroxide, though not a necessity of the soil for the best productivity, seems to be symptomatic, however, of strong vital soils, in which various soil factors, as suitable organic matter, bacterial activity, oxidation power, etc., are prominent. The relation between the strong, vital soils and the poor soils seems to be comparable to that found by Winternitz and Meloy [1] between normal tissue and diseased tissue in that in general the normal tissue had the greater catalytic power.

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[1] Jour. Exp. Med., **10**, 759 (1908).

RELATION BETWEEN THE OXIDIZING AND THE CATALYZING POWER OF SOILS.

In plants there seems to be a certain amount of association between the oxidizing and the catalyzing power. In soils it becomes of interest to see if the oxidizing power and the power to decompose hydrogen peroxide are correlated in any way. It was found that as a rule the soils with strong oxidizing power were the better catalyzers, while soils of poor oxidizing power were poor catalyzers. The relation between the two factors is not a direct one since the order of oxidation is not necessarily the order of catalysis as the following table shows:

TABLE II.—*Order of catalysis as compared with the order of oxidation.*

Soil.	Order of oxidation.	Order of catalysis.
Clarksville silt loam, Kentucky	1	1
Frankstown stony loam	2	3
Hagerstown loam plus manure	3	4
Wheeling gravelly loam subsoil	4	6
Wheeling gravelly loam soil	5	5
Clarksville silt loam, subsoil, Kentucky	6	2
Frankstown stony loam, subsoil	7	7

In the case of oxidation in the experiments already reported it was not possible to extract the oxidizing principle from the soil with water or glycerine. So in the case of catalysis no catalyzing principle could be extracted from the soils by water, glycerine, and dilute alkalies. Both the oxidizing principle and the catalyzing principle are probably present in the soil in not very great quantities and are absorbed by the soil to such an extent that it is not possible to extract them, or they are changed in the process of extraction.

The power of oxidizing easily oxidizable substances and the power to decompose hydrogen peroxide do not necessarily go hand in hand, since the addition of citric acid to certain soils increases the oxidative power while greatly decreasing the catalytic power. Again the oxidizing power may be lost while the catalyzing power is still present, though weakened. Thus the oxidizing power may be practically destroyed by using the soil several times in succession to oxidize aloin as brought out by the following experiments: Ten grams of soil were treated with 70 c. c. of a one-eighth per cent aloin solution. The mixture was then centrifuged and the supernatant oxidized aloin solution was poured off and the soil again treated with 70 c. c. of fresh aloin solution. After three oxidation tests in this way the soil had practically no power to oxidize the aloin. The same treatment was made with the soil and water only. The soils were then dried at the room temperature and 5 grams of each soil was tested

for its catalytic power in relation to the soil untreated.   The results are shown in Table III.

TABLE III.—*Effect of loss of oxidation and treatment with water on catalytic power of soil:* (A) *Catalytic power of soil deprived of oxidation power,* (B) *of soil treated with water as in the oxidation experiment,* (C) *of untreated soil.*

Soils.	Quantity of oxygen evolved in—					Time to evolve 40 c. c. of oxygen.	Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	145 minutes.			
Hagerstown loam plus manure:	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*Minutes.*	*Minutes.*	*Minutes.*
A	23	34	43	53	60	25	48.1	144
B	30	46	56	60	62	11.7	20	48.3
C	47	57	59	59	60	4.8	8.4	103
Hagerstown loam plus complete fertilizer:								
A	26	39	56	57	61	16.3	29.1	76
B	45	59	62	62	63	5.1	8.6	17.6
C	52	61	62	62	63	3.9	6.2	12.2
Hagerstown loam, lime, and manure:								
A	50	60	61	61	62	4.5	7	14
B	63	67	67.1	67.1	67.3	2.5	3.8	5.7
C	66	67.3	67.5	67.5	67.6	1.2	1.9	3.2
Hagerstown loam plus lime:								
A	57	66	66.7	66.7	67.2	3.1	4.8	9.6
B	55	65	75	75	75.7	3.3	5	9.8
C	67	68.3	68.6	68.6	68.8	1.7	2.7	4.6
Clarksville silt loam, Kentucky:								
A	61	66.3	66.3	66.3	....	2.7	4	6.4
B	65.5	65.7	65.7	65.7	....	1.1	1.6	2.8
C	65.5	66.5	66.5	66.4	....	1	1.3	2.2
Orangeburg loam:								
A	59	61	61.3	61.2	....	2.1	3.6	8.3
B	63	63	63.2	63.2	....	.8	1.2	2.5
C	62	62	62.4	62	....	.8	1.2	3

Treating the soil with water decreased the rate considerably in most cases, but by no means as much as treating with the same amount of aloin solution.   The loss of the oxidizing power, while markedly decreasing the rate of catalysis, had little effect on the total amount of oxygen evolved from the hydrogen peroxide.   There is some relationship between the forces bringing about the oxidation of easily oxidizing bodies and those decomposing hydrogen peroxide.

CATALYTIC POWER OF SUBSOILS.

In general, the subsoils are less productive than the surface soils. In studying the relation of oxidation to productivity it was found that the oxidation power of the subsoil, as a rule, was poor in comparison with that of the corresponding soil.[1]   In a less marked degree than in the case of oxidation, the catalytic power of the subsoil is less, as a rule, than that of the soil, as may be seen in Table IV.   These soils and subsoils were air-dried samples of soil, which had recently come from the fields.

[1] Bul. 73, Bureau of Soils, U. S. Dept. Agr., 1910.

TABLE IV.—*Catalytic power of soils and subsoils.*

Soils.	Quantity of oxygen evolved in—			Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.		
	C. c.	*C. c.*	*C. c.*	*Minutes.*	*Minutes.*
Clarksville silt loam, Kentucky:					
Soil	64	65	65	1.75	2.6
Subsoil	62	62	62	1.75	3.2
Frankstown stony loam:					
Soil	65	65	66	2.2	3.3
Subsoil	13	19	26	....	....
Dekalb silt loam:					
Soil	59	63	64	4	7.5
Subsoil	9	14	18	....	....
Wheeling gravelly loam:					
Soil	40	56	61	11	21
Subsoil	34	51	60	13.6	30
Amarillo silt loam:					
Soil	56	62	63	5	10
Subsoil	47	57	60	8	30
Dunkirk clay:					
Soil	16	22	27	....	....
Subsoil	35	49	55	8.8	15.5
Clyde loam:					
Soil	23	37	51	28	....
Subsoil	7	9	12	....	....
Decatur clay loam:					
Soil	68	69	69	3.6	....
Subsoil	54	63	66	11.3	....
Norfolk sandy loam:					
Soil	17	22	28	....	....
Subsoil	12	15	17	....	....
Cecil clay:					
Soil	39	50	54	15	....
Subsoil	29	50	56	14.5	....

The catalytic power of the recently dried samples of subsoil was less than that of the surface soil in 8 out of 10 cases. It is most probable that many factors which make for soil fertility are more prominent in soils than in subsoils. The reaction between the catalytic power of the soil and subsoil was then extended to samples of soil which had been in an air-dried condition in Mason jars for a number of years.

TABLE V.—*Catalytic power of soils and subsoils (old samples).*

Soils.	Collected.	Quantity of oxygen evolved in—						Time to evolve 30 c. c. of oxygen.	Time to evolve 40 c. c. of oxygen.	Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
		7 minutes.	15 minutes.	30 minutes.	45 minutes.	60 minutes.	90 minutes.				
		C. c.	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*Min.*	*Min.*	*Min.*	*Min.*
Dekalb silt loam:											
Soil	1906	52	60	62	62	62	62	2.3	3.6	6	14
Subsoil		6	8	12	14	16	19	....	....	....	....
Fayetteville loam:											
Soil	1907	53	61	62	63	64	65	2.5	3.6	5.8	11.5
Subsoil		11	18	27	35	41	48	35.5	58.3	100	....
Norfolk loam:											
Soil	1907	47	61	68	68	69	69	3	5.2	8.5	13.7
Subsoil		3	5	7	8	10	13	....	....	....	....
Wheeling gravelly loam:											
Soil	1906	55	60	63	63	63	63	3.6	5.6	8.9	15.2
Subsoil		35	52	59	61	61	61	5.3	9.1	13.7	34.5
Susquehanna fine sandy loam:											
Soil	1908	20	32	43	49	55	59	14	24.5	46.2	94.5
Subsoil		.....	.....	.....	1	2	4	....	....	....	....
Lufkin sand:											
Soil	1905	33	48	57	60	62	64	5.9	10.2	16.8	42.3
Subsoil		14	28	44	53	58	61	16.8	25.2	....	78

The table shows that the catalytic power persists more or less in the samples left in a dry condition in the laboratory for several years, and that in these old samples the catalytic power of the surface soils is greater than that of the subsoil. Since true enzymes, such as the amylolytic, proteolytic, and inverting enzymes, readily undergo decomposition, it seems rather unlikely that the catalytic power of the old samples of soils which had been for years in a dry condition in closed Mason jars is due to enzyme action. It may be said in passing, however, that Loew reported catalase in leaves of tobacco dried for many years, although other enzymotic activities were negative.
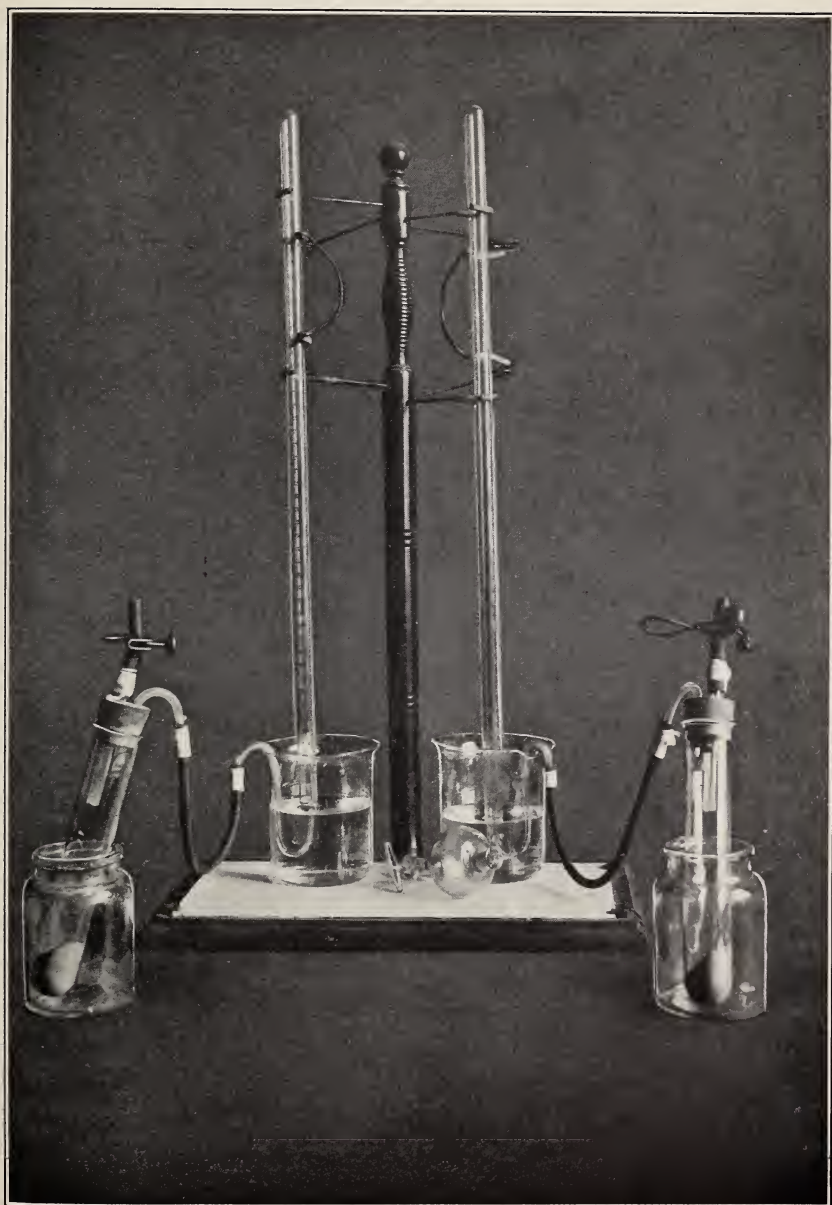
EFFECT OF FERTILIZERS AND PLANT GROWTH ON CATALYTIC POWER.

The air-dry samples of soils, Frankstown stony loam, Takoma Park soil, Amarillo silt loam, Westmoreland clay, Clarksville silt loam, and Dekalb silt loam, were treated with distilled water until the water content was 18 per cent of the air-dry soil. Then, on the basis of air-dried soil, $NaNO_3$, K_2SO_4, $CaH_4 (PO_4)_2$, and mixtures of equal parts of these three salts were added to the soils in the ratio of 50 pounds of NH_3, K_2O, and P_2O_5 per acre; manure in the ratio of 25 tons to the acre; manure and lime in the ratio of 25 tons of manure and 2 tons of lime ($CaCO_3$) to the acre; lime ($CaCO_3$) 2 tons to the acre; ground cowpeas, well rotted, 5 tons to the acre. The soils were placed in pots, two pots to each treatment, and wheat, six plants to the pot, was grown for 18 days; then the green weight of the plants was taken, and on the following day the sifted samples were tested for the oxidative power and two days later for their catalytic power. The results are given in Table VI:
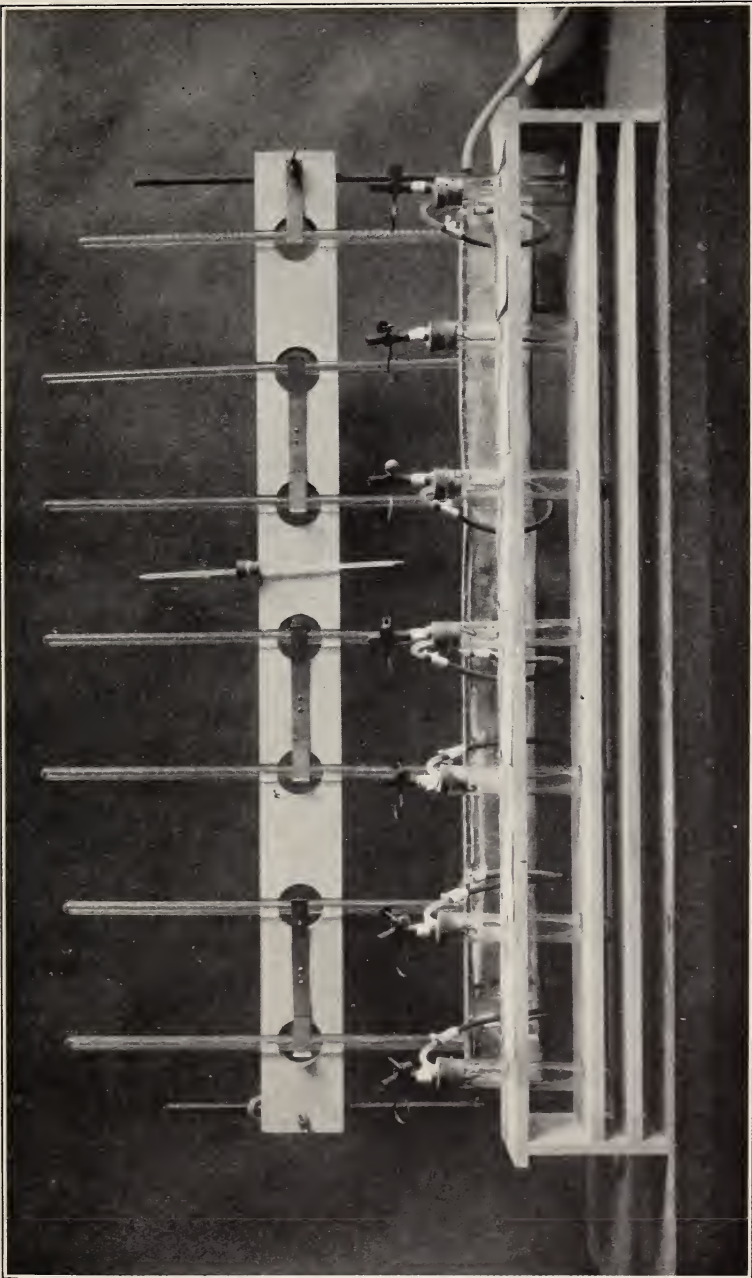
TABLE VI.—*Catalytic power of fertilized and planted soils.*

Soil.	Treatment.	Green weight of wheat.	Quantity of oxygen evolved in—				Time to evolve 40 c. c. of oxygen.	Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
			7 minutes.	15 minutes.	30 minutes.	60 minutes.			
		Grams.	C. c.	C. c.	C. c.	C. c.	Min.	Min.	Min.
Frankstown stony loam.	N.............	3.060	55	58	58	....	2.5	4.5	....
	K.............	3.330	58	62	62	....	2	3.6	10.5
	P.............	2.870	55	57	57	....	2.5	4.4	....
	NKP.............	2.748	53	57	57	....	3	5.5	....
	NKP.............	(1)	....	....	....	....	....	....	....
	Manure.........	3.605	55	60	60	....	2	3.4	10.5
	Manure and lime	3.260	56	58	58	....	2	3.6	....
	Lime...........	2.960	58	61	61	....	1.9	3.2	9.25
	Cowpeas........	3.432	58	60	60	....	1.9	3.3	14
	Check..........	2.790	57	60	60	....	2	3.3	10
	Check..........	(1)	57	61	61	....	2.25	4.6	12.6
Takoma lawn soil.	N.............	1.530	5	10	16	23	....	....	....
	K.............	1.690	5	9	13	14	....	....	....
	P.............	1.925	8	14	20	27	....	....	....
	NKP.............	2.106	6	11	17	24	....	....	....
	NKP.............	(1)	5	10	15	20	....	....	....
	Manure.........	2.545	8	13	21	26	....	....	....
	Manure and lime	4.115	12	20	27	36	....	....	....
	Lime...........	3.670	9	15	22	29	....	....	....
	Cowpeas........	3.230	10	16	24	29	....	....	....
	Check..........	1.980	5	9	15	19	....	....	....
	Check..........	(1)	5	9	15	20	....	....	....

[1] Not planted.

PLATE I.

APPARATUS FOR DETERMINING THE CATALYTIC POWER OF SOILS.

PLATE II.

IMPROVED FORM OF APPARATUS FOR DETERMINING THE CATALYTIC POWER OF SOILS.

TABLE VI.—*Catalytic power of fertilized and planted soils*—Continued.

Soil.	Treatment.	Green weight of wheat.	Quantity of oxygen evolved in—				Time to evolve 40 c.c. of oxygen.	Time to evolve 50 c.c. of oxygen.	Time to evolve 60 c.c. of oxygen.
			7 minutes.	15 minutes.	30 minutes.	60 minutes.			
		Grams.	C. c.	C. c.	C. c.	C. c.	Min.	Min.	Min.
Amarillo silt loam.	N	3.785	55	60	62	....	2.5	5	14
	K	3.615	53	59	61	....	3.6	5.8	20.5
	P	3.450	53	59	61	....	3.2	5.5	19.75
	NKP	3.670	52	56	59	....	3.3	6.25	18.5
	NKP	(1)	54	58	60	....	3.2	5.5	23.5
	Manure	3.450	53	58	62	....	3.3	6.1	19.2
	Manure and lime	3.455	54	59	62	....	3	5.25	17.4
	Lime	3.130	53	58	60	....	3.25	5.3	20.6
	Cowpeas	3.300	52	58	59	....	3.6	5.8	....
	Check	3.405	53	58	61	....	3.25	5.6	18.5
	Check	(1)	53	60	63	....	4.1	6	14.3
Westmoreland clay.	N	3.160	30	41	50	....	14.5	28.8	....
	K	3.290	27	39	50	....	15.8	29.3	....
	P	2.560	27	38	48	....	17	....	....
	NKP	2.060	26	37	46	....	18.75	....	....
	NKP	(1)	27	40	50	....	15.25	29.2	....
	Manure	3.035	30	40	51	....	15.3	27.5	....
	Manure and lime	3.610	32	43	56	....	12.2	21.3	....
	Lime	3.110	31	43	56	....	12.1	21	....
	Cowpeas	3.000	27	37	48	....	17.3	34	....
	Check	2.500	28	37	50	....	16.5	29.8	....
	Check	(1)	24	34	48	....	21.5	....	....
Clarksville silt loam, Kentucky.	N	3.300	59	61	....	....	1.6	2.8	9.25
	K	3.190	58	61	....	....	3.5	5	11
	P	3.112	61	61	....	....	1.6	2.6	5.80
	NKP	3.140	59	60	....	....	1.6	2.9	8.25
	NKP								
	Manure	3.270	58	63	....	....	2.1	4.2	7.5
	Manure and lime	3.390	60	62	....	....	1.3	2.25	6
	Lime	2.940	59	61	....	....	1.6	2.6	11.8
	Cowpeas	3.020	55	59	....	....	2.8	5.5	....
	Check	2.955	56	57	....	....	1.75	4.25	....
	Check	(1)							
Dekalb silt loam.	N	3.375	51	55	59	....	3.8	6.75	....
	K	3.500	52	57	62	....	3.6	6	19.5
	P	3.051	51	54	57	....	4	7	....
	NKP	3.450	50	54	56	....	4.2	7	....
	NKP		51	59	60	....	3.5	6.25	17.8
	Manure	3.420	52	56	59	....	3.5	6.75	....
	Manure and lime	3.140	54	59	62	....	3	5.1	19.5
	Lime	3.060	52	54	59	....	5.6	9.75	....
	Cowpeas	3.000	47	53	56	....	4.5	9.8	....
	Check	3.230	50	56	62	....	3.5	6.75	25
	Check		45	54	57	....	....	....	....

[1] Not planted.

The different fertilizers in conjunction with plant growth had different effects in the different soils. In the case of Frankstown stony loam the crop growth and the fertilizers had little effect on the catalytic power. In the case of Takoma lawn soil, manure and lime made a considerable increase in the total amount of oxygen evolved over the unplanted and planted checks. In case of Amarillo silt loam, the general trend of the effect of crop growth and fertilizer was to quicken the rate of catalysis slightly. In the case of Westmoreland clay the limed soils were the better catalyzers. In the case of the Dekalb silt loam, the soil containing lime and manure was the best catalyzer. It may be seen from the preceding table that the treat-

ment which gives the best growth does not necessarily give the greatest catalysis of the hydrogen peroxide.

EFFECT OF LIMING AND PLANTING ON THE CATALYTIC POWER.

To test the effect of lime on the catalytic power, wheat was grown in pots of Clarksville silt loam, fertilized with different ratios of the fertilizer salts (sodium nitrate, potassium sulphate, and acid calcium phosphate) so that the soil contained 50 pounds per acre of NH_3, K_2O, P_2O_5, or mixtures of these, and the limed portion in addition 2,000 parts of calcium carbonate per million of soil. The wheat was grown three weeks and the green weight of the plants was taken, and the soils were thoroughly sifted from roots, etc. After the soils had become air dry, the catalytic power was tested in the usual manner. As may be seen in the following table, the limed soils had a slightly quicker rate of catalysis. Whether the effect of liming on the catalytic power of the planted soil was direct or indirect is not known.

TABLE VII.—*Effect of lime on the catalytic power of a planted soil.*

Soil and treatment.	Ratio P–N–K.	Quantity of oxygen evolved in—		Time to evolve 40 c. c. of oxygen.	Time to evolve 50 c. c. of oxygen.
		7 minutes.	15 minutes.		
Clarksville silt loam, Kentucky:		*C. c.*	*C. c.*	*Minutes.*	*Minutes.*
Limed	10– 0– 0	67	68	0.91	1.33
Not limed		67	68	.97	1.4
Limed	3– 3– 4	70	71	.91	1.3
Not limed		68	69	1.13	1.6
Limed	0–10– 0	57	57	1.33	2.2
Not limed		56	56	1.71	2.9
Limed	0– 0–10	64	64	.97	1.5
Not limed		60	60	1.37	2.25
Limed	Check.	60	60	1.08	1.6
Not limed		62	62	1.23	2.0

EFFECT OF MOISTURE CONTENT ON THE CATALYTIC POWER.

In the case of oxidation by soils, the oxidizing power was increased by increase of water to optimum water content. To test the effect of moisture on catalysis, the water was added to each soil until the percentage of water based on the dry weight of the soil was 16. The soils were kept in this condition for two weeks and equivalent amounts of the moist and dry soils were compared. An increase in the moisture content of the soil decreased rather than increased the catalytic power, as may be seen in the following table:

TABLE VIII.—*Effect of moisture on catalytic power of soils:* (A) *moist soil,* (B) *air-dried soil.*

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.		
	C. c.	*C. c.*	*C. c*	*C. c.*	*Minutes.*	*Minutes.*
Sassafras silt loam:						
A	7	10	11	11		
B	9	12	16	18		
Clarksville silt loam, Tennessee:						
A	55	60	61	61	5.3	12
B	56	62	62	62	4.5	9.75
Hagerstown loam:						
A	50	56	56	56	6.8	
B	57	63	63	63	5.2	8.75
Hagerstown loam and manure:						
A	50	56	56	56	7	
B	50	60	63	63	7	14
Arlington clay loam:						
A	15	22	28	33		
B	15	22	27	33		
Sassafras clay loam:						
A	6	11	13	15		
B	7	15	26	38		

This effect of moisture would seem to throw out the possibility that the power of these soils to decompose hydrogen peroxide is due to a soluble catalase.

ACTION OF POISONS ON THE CATALYTIC POWER.

Carbon bisulphide.—May and Gile [1] found that the addition of 0.1 c. c. of carbon bisulphide to 5 grams of soil greatly depressed the catalytic power of Porto Rican soils. Accordingly, as in their experiments, 0.1 c. c. of carbon bisulphide was added to 5 grams of soil and the soil was well shaken. After the odor of bisulphide was no longer noticeable a test was made. The following table gives the results:

TABLE IX.—*Effect of carbon bisulphide on the catalytic power of soils:* (A) *check soil,* (B) *soil treated with carbon bisulphide.*

Soils.	Quantity of oxygen evolved in—			Time to evolve 60 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	
	C. c.	*C. c.*	*C. c.*	*Minutes.*
Hagerstown loam plus complete fertilizer:				
A	50.5	59.5	60	17.25
B	48	56	56	
Hagerstown loam plus lime and manure:				
A	54	60	60	10.5
B	64	67	67	4.5
Hagerstown loam plus lime:				
A	59	63	63	7
B	52	54	54	
Clarksville silt loam:				
A	72	74	76	3
B	81	81	81	1.75

[1] Loc. cit.

TABLE IX.—*Effect of carbon bisulphide on the catalytic power of soils: (A) check soil,
(B) soil treated with carbon bisulphide*—Continued.

Soils.	Quantity of oxygen evolved in—			Time to evolve 60 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	
	C. c.	*C. c.*	*C. c.*	*Minutes.*
Sharkey clay:				
A	52	65.5	65.5	9.5
B	49	53	53	....
Volusia silt loam:				
A	27	41	55	45
B	13	21	30.5	....
Hagerstown loam plus manure:				
A	57	65	67	8.6
B	56	63	63	9
Orangeburg loam:				
A	65	66	66	1.8
B	64	65	65	1.75
Woodland soil, Reading, Conn.:				
A	55	63	63	10.8
B	53	62	63	10
Dutchess loam:				
A	39	54	63	23.5
B	35	50	59	34.6

The table shows that the carbon bisulphide has a retarding effect on
the amount of catalysis and considerably reduces the rate in most
cases. In two cases, Hagerstown loam plus lime and manure and
Clarksville silt loam, treatment with carbon bisulphide greatly
increased the catalytic power of the soil. It would seem that the
catalytic power of soils is due to different causes in different soils.

Mercuric chloride.—Mercuric chloride has a greater retarding action
on catalysis than carbon bisulphide. When added to soil in the
proportion of 0.5 c. c. of a 1 per cent solution to each 5 grams of soil
mercuric chloride markedly decreases the rate of catalysis, in some
cases to less than half the rate of the untreated soil. The effect of the
mercuric chloride on the absolute amount of oxygen evolved is not
marked and in two cases, Orangeburg loam and Clarksville silt loam,
Kentucky, it had practically no effect on the rate. With increasing
amounts of mercuric chloride, the rate of catalysis is in general still
further lessened.

Hydrocyanic acid.—Hydrocyanic acid checks the catalytic power of
both the enzyme β-catalase and the inorganic colloidal solutions.
Upon Loew's insoluble α-catalase it had little action. To test the
effect of the hydrocyanic acid on soils 10 c. c. of a 2 per cent solution
of the acid were allowed to stand over night on 5 grams of soil which
had recently come to the laboratory from the field. To the check
soils 10 c. c. of distilled water were added. Then 5 c. c. of full
strength neutralized hydrogen peroxide were added and the oxygen
collected with the results as shown in Table X.

TABLE X.—*Effect of hydrocyanic acid on total amount of oxygen evolved and on rate of evolution: (A) check soil, (B) soil treated with hydrocyanic acid.*

Soils.	Quantity of oxygen evolved in—							Time to evolve 40 c. c. of oxygen.	Time to evolve 50 c. c. of oxygen.	Time to evolve 60 c. c. of oxygen.
	7 min-utes.	15 min-utes.	30 min-utes.	60 min-utes.	90 min-utes.	140 min-utes.	300 min-utes.			
	C. c.	C. c.	C. c.	C. c.	C. c.	C. c.	C. c.	Min.	Min.	Min.
Hagerstown loam plus manure:										
A	42	55	60	62	63	64	64	6.5	10.75	29.5
B	5	10	18	29	38	45	55	98.5	155	....
Hagerstown loam plus complete fertilizer:										
A	44	55	58	58	58	58	58	5.75	10	....
B	7	15	25	38	47	53	59	65	124	....
Hagerstown loam plus lime and manure:										
A	53	59	60	60	60	60	60	4.5	5.8	20
B	23	40	54	61	61	61	62	14.75	22.7	49.5
Hagerstown loam plus lime:										
A	50	57	58	59	59	59	59	4.3	7	....
B	26	44	57	63	64	64	64	12.8	19	37
Orangeburg loam:										
A	60	62	62	63	63	64	64	2.25	2.9	6.5
B	36	49	53	59	64	65	65	8.25	16.7	45
Woodland soil, Reading, Conn.:										
A	38	54	60	61	61	60	60	7.5	11.3	23.7
B	6	12	22	38	47	52	60	64	104	180
Dutchess loam:										
A	27	41	54	62	62	62	62	13.8	23.5	44.8
B	4	9	17	28	34	42	43	122.5	....	....
Volusia silt loam:										
A	11	19	28	38	44	52	58	71	130	....
B	1	3	5	10	12	15	16	....	....	....
Clarksville silt loam:										
A	59	61	61	62	61	60	60	2.6	3.8	7.2
B	36	52	58	61	60	59	59	8.25	13.2	37.3
Amarillo silt loam soil:										
A	22	34	42	48	50	51	52	23.6	84	....
B	.5	.5	.7	.8	.8	2.2	3	....	....	....
Amarillo silt loam subsoil:										
A	21	32	41	47	50	51	51	28.6	83	....
B	.5	1.3	2.3	4.4	6.3	7.9	8.5	....	....	....
Dekalb silt loam soil:										
A	28	41	48	51	51.1	51.5	51.8	14.5	42.5	....
B	2	3	5.5	9	12	17	19	....	....	....
Dekalb silt loam subsoil:										
A	3	5	8	12	14	19	27	....	....	....
B										
Frankstown stony loam soil:										
A	43	52	55	55	55	55	55	5.5	11	....
B	6.5	15	26	37	42	45	48	72.3	....	....
Frankstown stony loam subsoil:										
A	4	7	11	16	19	23	25	....	....	....
B	....	.2	.3	.8	.9	1.5	2	....	....	....

The hydrocyanic acid greatly retarded the catalysis but did not completely destroy the catalytic power. In soils like the Amarillo silt loam, soil and subsoil, Dekalb silt loam, subsoil, and Frankstown stony loam, subsoil, the hydrocyanic acid brought the catalytic power practically to a standstill.

In order to find out whether or not the soil recovered from the effect of the hydrocyanic acid three soils, a fair catalyzer, a good catalyzer, and a very good catalyzer, Volusia silt loam, Hagerstown loam, manured, and Orangeburg loam, respectively, were treated with 10 c. c. of a 2 per cent solution of hydrocyanic acid and were then spread out and exposed to draft from an electric fan until air dried and kept in air six days with frequent sifting until the odor of hydrocyanic acid was no longer detectable and no test for cyanide

could be obtained in the water extract. Then the air-dried soils which had been treated with the hydrocyanic acid were compared as regards their catalytic power with nontreated air-dried soils, and it was found that the injurious action of the hydrocyanic acid still persisted. The retarding effect of hydrocyanic acid seems to be due then not to the formation of a surface film as suggested by Bredig and Ikeda [1] and Kastle and Loevenhart,[2] but rather to its chemical action on soil constituents.

Hydrogen sulphide.—Schönbein [3] found that plant juices instantly lost their catalytic power upon coming in contact with hydrogen sulphide. Bredig and von Berneck [4] pointed out that hydrogen sulphide greatly retarded the catalytic action of platinum on hydrogen peroxide and in medium concentration, $\frac{M}{3450}$ practically brought the catalytic action of the platinum to a standstill. Loew [5] showed that soluble catalase of tobacco was injured by saturated aqueous solution of hydrogen sulphide but was not destroyed by it. To test the effect of hydrogen sulphide on the catalytic power of soil, 5 grams of soil were exposed to the gas in a bell jar for one hour. Then, after exposure to the air for 2 hours, the catalytic power of the soil was tested.

As in the case of platinum and the enzyme catalase, hydrogen sulphide has a great inhibiting action on the catalytic power of soils, a greater effect, in fact, than carbon bisulphide and mercuric chloride.

Phenol and alcohol.—According to Bredig and von Berneck,[5] phenol has little retarding effect on the catalytic action of platinum. In the case of soils, phenol has a varying effect. In some soils it has a slight retarding action, in others it retards considerably. In the case of Clarksville silt loam it had no effect whatever and in the case of Orangeburg loam it quickened the rate of catalysis slightly. Alcohol had practically no effect on the amount of oxygen evolved and reduced the rate of catalysis only to a moderate degree.

Hydrocyanic acid, mercuric chloride, carbon bisulphide, and hydrogen sulphide check the catalytic power of nonenzymotic substances as well as the catalytic power of the enzyme catalase. Accordingly the experiments with these anticatalytic substances throws little light on the nature of the catalytic power of soils, although from the fact that the catalytic power persists to a considerable degree in the presence of these antienzymotic substances especially in the presence of mercuric chloride and carbon bisulphide, it must be concluded that the catalytic power is due at least in part to other factors than the enzyme catalase. How much of the catalytic power of the

[1] Zeit. phys. Chem., **37**, 1 (1901).
[2] Amer. Chem. Jour., **29**, 397 (1903).
[3] Jour. prakt. Chem., **89**, 340 (1863).
[4] Zeit. phys. Chem., **31**, 258 (1899).
[5] Loc. cit.

soils is to be attributed to the various factors may be brought out by other experiments.

EFFECT OF HEAT ON THE CATALYTIC POWER.

Dry heat.—To test the effect of dry heat on the catalytic power of the soils, 5 grams of soil were placed in the air oven at 105° C. for an hour. Then 10 c. c. of $1\frac{1}{2}$ per cent neutralized hydrogen peroxide were added to the soil and the oxygen collected in the usual manner. The results are shown in Table XI.

TABLE XI.—*Effect of dry heat 105° C. on the catalytic power of soils: (A) check soils, (B) heated soils.*

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	
	C. c.	*C. c.*	*C. c.*	*C. c.*	*Minutes.*
Hagerstown loam plus manure:					
A	49	57	57	57	7. 6
B	39	47	49	49	....
Hagerstown loam plus complete fertilizer:					
A	48	55	55	55	8. 5
B	·43	56	58	59	10. 2
Hagerstown loam plus lime and manure:					
A	56	57	57	57	4
B	56	57	57	57	4. 3
Hagerstown loam plus lime:					
A	60	61	61	61	3
B	55	57	57	57	5. 25
Hagerstown loam untreated:					
A	53	59	59	59	5. 5
B	44	55	56	56	10. 25
Clarksville silt loam, Tennessee:					
A	57	64	65	65	5
B	55	61	61	61	5. 3
Sharkey clay:					
A	53	60	60	60	6
B	54	61	61	61	5. 6
Volusia silt loam:					
A	26	39	51	57	28
B	9. 0	15	20	24	....
Dutchess loam:					
A	45	53	61	62	13
B	34	44	57	63	20
Woodland soil, Reading, Conn.:					
A	58	61	62	62	5
B	14	22	32	39	159
Orangeburg loam:					
A	61	61	61	61	1. 2
B	63	64	64	64	1. 2
Frankstown stony loam:					
A	60	65	65. 7	65. 8	4. 8
B	43	58	64	64	10
Amarillo silt loam soil:					
A	53	63	74	75	5. 6
B	46	59	73	75	9. 2
Amarillo silt loam subsoil:					
A	55	63	65	65. 5	5. 2
B	51	62	66	67	7. 5

The effect of dry heat is in general to lessen the catalytic power of the soil. In some soils, as may be seen in the table, dry heat had practically no effect on catalysis, while in others it caused a marked decrease in the catalytic power. In general, the results from dry soils agree with those of May and Gile, who found that heating for one-half hour at 100° C. destroyed only two-tenths of the active amount of catalase, and that heating for several hours diminished the activity

less than half. From the fact that in certain cases, such as Volusia silt loam, the decomposition of the hydrogen peroxide goes on for a certain length of time and to a certain degree and then stops entirely suggests that, contrary to our expectation, the decomposing power is not due to catalase, but rather to definite chemical substances which are more or less destroyed or changed by heat. The retarding effect both of heat and of substances which check catalysis is more noticeable in soils which have naturally only a slight catalytic power.

Steam heat.—The soils in tubes plugged with cotton were heated in a steam sterilizer for 1 hour and 15 minutes. Then the catalytic power was tested in the usual manner.

The effect of steam heat in reducing the catalytic power of the soils is only slightly greater than that of the dry heat.

Heating under pressure.—Heating the soils in an autoclave for one hour at a pressure of 10 atmospheres had a marked inhibiting action on the catalytic power of the soil, as the following table shows:

TABLE XII.—*Effect of heating under pressure on the catalytic power of soils: (A) check soil, (B) heated soil.*

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	
	C.c.	*C.c.*	*C.c.*	*C.c.*	*Minutes.*
Hagerstown loam plus manure:					
A	47	56	59	60	8.5
B	6	9	13	17	....
Hagerstown loam plus complete fertilizer:					
A	50	59	60	61	7
B	5	9	14	23	....
Hagerstown loam plus lime and manure:					
A	55	57	57	57	4.25
B	17	25	32	35	....
Hagerstown loam plus lime:					
A	60	64	65	65	4.75
B	13	19	26	30	....
Hagerstown loam untreated:					
A	49	58	59	59	7.6
B	8	13	19	24	....
Clarksville silt loam, Tennessee:					
A	50	56	57	57	6.8
B	4	9	11	11	....
Sharkey clay:					
A	56	58	58	59	4.75
B	6	9	18	34	....
Volusia silt loam:					
A	27	41	51	55	27.5
B	4	4	4	4	....
Amarillo silt loam soil:					
A	62	65	65	65	3.4
B	39	46	51	53	21
Amarillo silt loam subsoil:					
A	56	64	66	66	5.5
B	40	52	59	62	13
Frankstown stony loam:					
A	62	64	64	65	3.2
B	7	11	16	23	....
Dutchess loam:					
A	44	58	63	63	10
B	18	24	33	45	....
Woodland soil, Reading, Conn.:					
A	50	57	57	57	7
B	6	8	11	17	....
Orangeburg loam:					
A	60	60	60	60	1.4
B	56	60	60	60	4

Catalase has been reported in plants and in microorganisms. Naturally it would be expected to be in soil. If, however, the catalytic power of the soils tested by us is due to an enzyme, the enzyme must have a wonderful resistance to heat, since soils heated to 180° C. in the autoclave for one hour still have considerable catalytic power. Guisti [1] found that heating in an autoclave to 133° C. destroyed the catalytic power of all microorganisms, while it has been found [2] generally that plant catalase is less resistant. As shown by Loew both α and β catalase are destroyed by heating to 75°–80° C.

Ignited soils.—König and his coworkers and likewise May and Gile found that ignited soils had very little power to decompose hydrogen peroxide. To study the effect of ignition, the soils in the following table were weighed out and were heated to a red heat. When cold the catalytic power was determined. As the table shows, the ignited soils had, as a rule, a fair decomposing action on the hydrogen peroxide, a stronger action for the most part than did the same soils steam-heated under pressure. Only five soils suffered a marked loss of catalytic power, namely, Sharkey clay, Volusia silt loam, Amarillo silt loam, Amarillo silt loam, subsoil, and Woodland soil.

TABLE XIII.—*Effect of ignition on the catalytic power of soils: (A) normal soil, (B) ignited soil.*

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	
	C. c.	*C. c.*	*C. c.*	*C. c.*	*Minutes.*
Hagerstown loam plus manure:					
A	50	59	61	61	7
B	29	43	55	62	21.6
Hagerstown loam plus complete fertilizer:					
A	53	61	62	62	6
B	31	45	55	60	19.3
Hagerstown loam plus lime and manure:					
A	57	58	58	58	3.6
B	45	57	57	57	10
Hagerstown loam plus lime:					
A	63	64	64	64	3
B	55	61	61	61	5.3
Hagerstown loam:					
A	53	59	61	61	5.3
B	31	45	55	55	20
Clarksville silt loam, Tenn.:					
A	49	55	56	56	7.3
B	30	42	51	54	26
Sharkey clay:					
A	64	68	68	68	3
B	8	16	26	39	....
Volusia silt loam:					
A	30	44	57	62	21
B	6	10	17	24	....
Amarillo silt loam, soil:					
A	62	65	68	65	3.4
B	9	15	23	34	135
Amarillo silt loam, subsoil:					
A	56	64	66	66	5.5
B	6	12	22	36	112
Frankstown stony loam:					
A	62	64.8	64.8	65	3
B	19	29	41	54	48

[1] Annali di Medicina Navale, **10**, II, 213 (1908).
[2] See Die Katalase. F. Battelli and L. Stern. Ergebnisse der Physiologie, **10**, 546 (1910).

TABLE XIII.—*Effect of ignition on the catalytic power of soils: (A) normal ·soil, (B) ignited soil*—Continued.

Soils.	Quantity of oxygen evolved in—				Time to evolve 50 c. c. of oxygen.
	7 minutes.	15 minutes.	30 minutes.	60 minutes.	
	C. c.	*C. c.*	*C. c.*	*C. c.*	*Minutes.*
Dutchess loam:					
A	44	58	63.3	63.8	10
B	38	54	63	65	12.3
Woodland soil, Reading, Conn.:					
A	50	57	57	57	6.9
B	4	6	9	14	....
Orangeburg loam:					
A	60	60	60	60	1.4
B	44	53	58	58	11

The catalytic power of the ignited soils is due altogether to the inorganic constituents. In the normal soil the catalytic power is due only in part to the inorganic matter, since heating in the autoclave under pressure, a treatment which greatly decreases the catalytic power, would not make much change in the inorganic matter, as compared with the organic matter of the soil, and would most probably destroy the enzyme catalase if it were present. Incinerating the soil would convert some of the salts to oxides and would make the medium slightly alkaline, conditions which favor the decomposition of the hydrogen peroxide.

EFFECT OF INCREASING TEMPERATURES ON THE CATALYTIC POWER.

Soils were kept one hour at temperatures ranging from 30° to 140° C. Then after cooling to the room temperature, the rate of catalysis was tested. The results are shown in Table XIV.

TABLE XIV.—*Effect of increasing temperature on the rate of catalysis. The catalytic power of all soils was tested at room temperature.*

Soil.	Time required to evolve 50 c.c. of oxygen at—						Temp. of maximum rate.
	30° C.	65° C.	95° C.	110° C.	125° C.	140° C.	
	Min.	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	° C.
Dekalb silt loam	5	4.2	5.8	7.2	16	20.5	65
Frankstown stony loam	3	3	4.8	6.1	10	14.7	30–65
Hagerstown loam plus manure	5	5.7	7	6	21	17.2	30
Clarksville silt loam	1.7	1.2	1	1.5	2.2	3.1	95
Amarillo silt loam	6	4.7	5.6	5.8	13	7.1	65
Woodland soil, Reading, Conn	4.1	4.5	13.8	22	71.5	51.3	30
Volusia silt loam	57	89	180	......	......	......	30
Dutchess loam	9.7	10.5	14.8	18	20.7	21	30–65
Orangeburg loam	.83	1.0	.91	1.3	1.1	1.1	30–95
Hagerstown loam plus lime	2.5	1.8	2.6	3.2	3.1	2.6	· 65
Hagerstown loam	1.8	2.2	2.8	3.4	3.3	3	30

In the case of the Dekalb silt loam, Hagerstown loam plus lime, Clarksville silt loam, and Amarillo silt loam, heating to 65° and cooling again to room temperature increased the catalytic power

of the soils.   Heating to 110° in the case of Amarillo silt loam and Clarksville silt loam increased the rate of catalysis, while heating Hagerstown loam plus lime to 95° had no decreasing action on the catalytic power.   The effect of heating the soil must have been upon the organic matter of the soil, since heating in this way would have no effect on the inorganic matter and would affect the catalase injuriously rather than otherwise.   In the case of Orangeburg loam, heating to 140° C. had little effect on catalysis, so in this soil also there is little probability that the catalytic power is due to catalase. In the case of the six other soils, it is possible that the catalytic power is due to catalase, though in no case was there a total destruction of the catalytic power.   Even in cases where heat retarded there is a secondary quickening of the rate of catalysis, in that the rate of catalysis, though slow, is greater after the soils have been heated to 140° C. than it is after they have been heated to 125°. In the case of the Hagerstown loam plus manure, heating to 110° has practically no retarding effect.

Catalytic power at different temperatures.—The catalytic power of the six soils which had their catalytic power lessened by heating to 65° for one hour was next tested at temperatures from 0° C. to 90° C.   The soil and the hydrogen peroxide were brought to the desired temperature before the peroxide was added to the soil. The results are shown in the following table:

TABLE XV.—*Effect of increasing temperatures on the rate of catalysis, i. e. the time required to evolve 50 c.c. of oxygen.   The catalytic power was determined at the temperature indicated.*

Soil.	Time required to evolve 50 c.c. of oxygen at—									
	2° C.	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
	Min.	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*
Hagerstown loam plus manure	10.1	6.7	3.1	2.1	1.2	1.1	1.1	0.6	0.5	0.2
Dutchess loam................	132	60	33.2	14.7	10.3	5	3.3	2.5	1.3	.86
Frankstown stony loam......	25.6	14	6.6	3.2	2.3	1.7	1.20	.64	.49	.51
Orangeburg loam.............	4.3	2.88	1.9	1.5	.60	.36	.32	.19	.14	.09
Volusia silt loam, virgin soil:										
A............................	84	47	35	27.7	23.7	32	36	28	7	2.5
B............................	148	70	58	54.9	52	(¹)	(¹)	34.6	12.3	3.7
Volusia silt loam, planted soil.	170	53	36.5	27.7	25.7	21	16.7	8.6	5.4	2

¹ At 50° and 60° no 50 c.c. reading could be obtained, so the readings are given for 40 c.c. (A) and 50 c.c. (B) for the series 2°–90° for Volusia silt loam, virgin soil.   In the case of this soil the catalytic power both as regards the total amount of oxygen evolved and the rate of evolution is less at 50° and 60° than at 30°. From 0° to 40° the rate of catalysis is quickened.   From 40° to 60° there is a falling off in the rate.   Above 60° the rate of catalysis is again markedly quickened.

It may be seen from the table that the rate of decomposition of the hydrogen peroxide by the soil is quickened by increasing the temperature with an exception of a break in the case of Volusia silt loam, virgin soil, and that no optimun temperature is apparent. The increased catalytic power with increase of heat up to 90°, beyond which temperature the experiment was not carried, indicates

that the catalytic power of these soils is not due to the enzyme catalase, unless the soil strongly protects the catalase from the injurious action of heat. The catalytic power of the eleven soils of Table XIV and Table XV seems to be due then not to enzymotic activity but to the organic and inorganic constituents of the soil.

That inorganic substances would act catalytically has long been known. The catalytic power of inorganic material was early pointed out by Thénard, and especially by Schönbein, and has been studied in detail by Bredig and his co-workers. Recently it has been pointed out by Bordas and Touplain [1] that colloidal ferrous oxalate or ferric lactate are found to give all the catalytic reactions of curdled milk.

CATALYTIC POWER OF SOILS AS RELATED TO THE MANGANESE CONTENT.

The catalytic power of a number of soils analyzed for their inorganic content by W. O. Robinson of this bureau were tested for their catalytic power. The catalytic power stood in very little relation with the Fe_2O_3 content, but did stand in close relation with the manganese content, estimated as MnO, as may be seen in the following table:

TABLE XVI.—*Catalytic power of soils in relation to their manganese content.*

Soils.	Content of MnO.[a]	Order of MnO content.	Order of catalysis 5 grams soil.	Order of catalysis 10 grams soil.	Time to collect 50 c.c. oxygen from 10 grams soil.	Quantity of O_2 collected from 10 grams soil in 60 minutes.
	Per cent.				*Minutes.*	*Cu. cen.*
Cecil clay soil	0.305	1	1	1	0.9	61
Decatur clay loam soil	.070	2	2	2	2.25	63.5
Decatur clay loam subsoil	.053	3	3	3	7.3	61
Cecil clay subsoil	.031	4	7	8	....	16.5
Cecil sandy loam soil	.029	5	5	5	97	41
Volusia silt loam subsoil	.026	6	6	6	....	24.5
Cecil sandy loam subsoil	.018	7	12	12	....	5.5
Durham sandy loam soil	.017	8	10	11	....	10
Durham sandy loam subsoil	.014	9	9	9	....	13
Volusia silt loam soil	.012	10	4	4	19.6	58
Norfolk sandy loam soil	.008	11	8	7	....	23.8
Norfolk sandy loam subsoil	.004	12	11	10	....	11

a Analyses by W. O. Robinson of this bureau, made in connection with a general study of inorganic soil constituents of prominent soil types, the results of which will be published later.

That the catalytic power of the soil is correlated to some degree with the manganese content of the soil is evident. It is the form of manganese rather than the absolute amount since Volusia silt loam with a small manganese content is a much better catalyzer than Cecil clay subsoil with two and one-half as much MnO, and since further, the addition of manganese salts, such as chloride, carbonate,

sulphate, and dioxide had no effect in increasing the catalytic power of soils. Some other factors than the total amount of manganese must be the determinants in producing the catalytic power of the soils. These factors are the nature of the manganese compound or the nature of the associated organic matter.

CATALYTIC POWER OF SOILS AS RELATED TO THE ORGANIC CONTENT.

In regard to the organic matter of the soil it may be said that König found that the catalytic power of the soils studied by him and his associates was in almost exact relationship to the humus content. In our work this relationship does not seem to obtain. Thus in Table XVI the best catalyzer, Cecil clay, has much less organic matter than Cecil sandy loam, which is a rather weak catalyzer. Further, in samples of Hagerstown loam from the plot experiments of the Pennsylvania State Experiment Station, which had been under the same treatment for a number of years, the limed and manured soil and the limed soil had a much smaller humus content and a considerably greater catalytic power, as may be seen in the following table. The humus was determined by extracting 20 pounds of soil with 15 liters of 2 per cent caustic soda[1] and precipitating the solution with dilute hydrochloric acid.

TABLE XVIII.—*Catalytic power of samples of Hagerstown loam of different humus content.*

	Hagerstown loam.	Hagerstown loam plus lime.	Hagerstown loam plus lime and manure.	Hagerstown loam plus complete fertilizer.	Hagerstown loam plus manure.
Humus content, in grams	43.63	11.33	5.53	30.50	30.33
Number of minutes required to evolve 50 c. c. of oxygen	7.6	4.75	4.25	7.0	8.5

As shown in Tables XI and XII the samples of Hagerstown loam as well as other soils had their catalytic power reduced by heating for one hour at 105° C. and especially by heating in an autoclave for an hour under a pressure of 10 atmospheres. It is obvious that the organic matter plays some part in the decomposition of hydrogen peroxide since the dry heating would have practically no effect on the inorganic matter and heating in the autoclave would have little effect on the inorganic as compared with the organic matter which suffers great change. It is the nature of the organic matter and not the absolute amount that is of importance.

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[1] See The Forms of Organic Nitrogen in plats 20–24. B. E. Brown and E. C. Lathrop. Report Penn. State College. 1909–10. 118.

CATALYTIC POWER OF ORGANIC SUBSTANCES.

Since no reference could be found relative to the action of definite organic substances on hydrogen peroxide, a number of organic compounds, 70 in all, were tested. Of these compounds, solanine, darkened pyridine, and darkened piperidine, especially the latter, possessed the direct power to decompose the hydrogen peroxide. Samples of solanine which had been exposed to the air but a short time had no action on the hydrogen peroxide until nicotine was added. Colorless pyridine likewise had no action on hydrogen peroxide. It would seem that the catalytic power of the organic compounds was due to a change brought about by partial oxidation as in the case of the old sample of solanine and the partially oxidized pyridine and piperidine. Pyridine, colorless or colored, has a slight activating action on the catalytic power of manganese dioxide while darkened piperidine greatly increases the power of manganese dioxide to decompose hydrogen peroxide. In the vast complex of organic matter of the soil it is to be expected that bodies would be present which would exercise a direct action on the hydrogen peroxide or an indirect action in activating other compounds, organic or inorganic, as the case may be.

As yet no catalyzing agent has been extracted from soils. In the case of Clarksville silt loam, however, there was isolated from the coarse sand from the mechanical analysis of this soil a considerable amount of black particles. These particles decomposed hydrogen peroxide, liberated chlorine from hydrochloric acid, and consisted undoubtedly of manganese dioxide. In the case of Volusia silt loam, Frankstown stony loam, and Sassafras silt loam no manganese dioxide was isolated by the mechanical separation method. Manganese dioxide alone, however, has by no means the same action on hydrogen peroxide as has a soil containing an equivalent amount of manganese calculated as MnO.

If the heat resisting catalytic power of soil is due to catalase, which must arise from plant or microorganisms, our conclusions must be like those of May and Gile, that the catalytic power of the soil is a rough measure of the combined quantity of bacteria and organic matter present in the soil. Unless the soil has a great protective power against the injurious effect of heat on enzymes, however, it would seem that the catalytic power of the soils studied by us is not due to an enzyme but rather to the inorganic and organic matter, working separately, conjointly, or in activating combinations in which the inorganic matter, especially manganese, is the active complement and the organic matter the activating complement.

The part that microorganisms play in the formation of activating substances and of compounds directly capable of decomposing

hydrogen peroxide is undoubtedly very great, but can not be considered in detail here.

SUMMARY.

Soils possess the power to decompose hydrogen peroxide. This power is greater in soil than in subsoils, in strong vital soils than in weak soils. It persists for years in air-dried soils.

Though good production is not dependent on the catalytic power, the presence of a strong catalytic power in a soil can be taken as a priori evidence that the many factors making for soil fertility would be prominent and that the soil would be a productive soil.

The catalytic power is checked to some degree by carbon bisulphide, mercuric chloride, and especially by hydrocyanic acid, which in some cases practically destroys it.

Heating in an autoclave under pressure of 10 atmospheres retards the catalytic power, though dry heat for one hour at 105° has little depressing action.

Various inorganic substances and several organic compounds, especially those in a state of partial oxidation, have the power of decomposing hydrogen peroxide, while several organic compounds increase the catalytic power of manganese dioxide.

In general the catalytic power of soils seems to be due not to an enzyme, such as catalase, but rather to the inorganic and organic matter working separately, conjointly, or in activating combination.

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